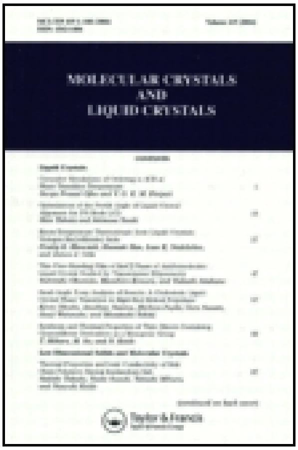

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# The Study of the Guest Effect on the Nematic Phase Stabilization

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# The Study of the Guest Effect on the Nematic Phase Stabilization

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The effect of azo-dye on some optical and thermodynamical properties of the liquid crystal 5CB are examined. The relation between molecular geometry of the guest, guest and host order parameters and nematic–isotropic transition temperature of the azo-dye/liquid crystal mixtures is determined. The experimental results are compared in some detail with calculations done on the basis of the molecular mean-field theory and predictions of the lattice models as well. It has been found that good agreement between experiment and theory can be obtained taking into account not only the molecular sizes of the solute and the guest–host interaction, but also the concentration dependence of the dye order parameter and the flexibility of the end-chain of the liquid crystal molecules.

*Keywords: guest–host systems, azo-dyes, order parameter, phase transition temperature*

## 1. INTRODUCTION

The liquid crystal display devices utilizing guest–host effect[1-5] are recently widely applicable because of displaying of information in color and wide viewing angle as well. However, in order to construct a competitive display with the conventional twisted nematic one, a number of factors must be taken into consideration.

It is well known, that addition of non-mesomorphic solute to the nematic liquid crystal changes the normal nematic–isotropic phase transition temperature, causing in most cases its decreasing.[6-12] However, such cases have been also reported, that a guest dissolved in liquid crystal stabilizes the nematic solvent leading to the increase of the clearing point.[13-19]

It has been also previously found, that a guest added to liquid crystal affect the host orientational order[12,20] and furthermore, the orientation of both liquid crystal and guest molecules depends on the solute concentration.[12,19,21,22]

In this paper the azo-dyes influence on the liquid crystal orientational order and on the phase transition temperatures as well as the dependence of the molecular order and the mesophase existence region on the guest concentration have been studied. The attempt of the investigation of the correlation between the geometry of guest molecules, degree of molecular order and nematic–isotropic transition temperature of the azo-dye/liquid crystal mixture has been also undertaken.

Azo-dyes are however not enough stable of UV light, but due to their other advantages (high extinction coefficients, availability of almost all shades, good solubility) they seem to be suitable for the majority of applications that do not call for continuous exposure to light. The most of azo-dyes have relatively high order parameter,[23-26] which prefer they to use in liquid crystal display devices. Moreover, it has been shown, that also azo-dyes with small order parameter can find application in some types of multicolor displays.[21,27]

## 2. MATERIALS AND METHODS

The commercial liquid crystal 5CB-*p*-pentylo-*p*'-cyanobiphenyl (K15, Merck) without further purification was used as a host, while several azo-dyes with various molecular sizes and shapes were used as guests. Additionally, one stilbene-dye was taken to studies. The dye I (D2) was obtained from BDH, all the other dyes were synthesized and chromatographically purified in Institute of Dyes, Łódź Technical University.

In Table I the molecular structure, the wavelength of the absorption maxima $\lambda_{max}$, the molecular weight M and the ratio of length to breadth i/d for the investigated dyes are shown. The sizes of the dyes were estimated from the known bond lengths and configuration in molecules[28] including the van der Waals radii of the terminal atoms.[29]

The order parameters of the dyes $\langle P_2 \rangle_G$ in the liquid crystal were evaluated basing on the dichroic ratios of absorption.[30] The polarized absorption spectra were measured using a Cary-17 spectrophotometer equipped with polarizers. The measurements were made in oriented "sandwich" cells of 7.5 μm in thickness. Temperature of the cells, changed from 25°C to 40°C was controlled with an accuracy of ±0.1°

by circulating water in the heating jacket from the thermostat. The planar orientation of liquid crystal and dye molecules had been achieved by treatment of the glass surfaces of cells with polyimide and by rubbing process additionally. This procedure gives a good homogenous orientation of liquid crystal molecules in thin layer what has been controlled with the aid of crossed polarizers.

The order parameter of the nematic host $\langle P_2 \rangle_H$ with and without dye was determined from refractive indices measured as a function of temperature. The measurements were made for sodium D light by use of a Leitz-Jelley microrefractometer with rubbing-induced homogenous alignment of the liquid crystal molecules. The Vuks approximation[31,32] assuming the internal polarization field to be of the Lorentz–Lorenz type was applied. The extrapolation to absolute zero which is required to extract order parameter from refractive index data[33] was performed by plotting $\log[(n_e^2 - n_o^2)/(\bar{n}^2 - 1)]$ against $\log[1 - T^*]$, where $T^*$ is reduced temperature and $\bar{n}^2 = \frac{1}{3}(n_e^2 + 2n_o^2)$. The uncertainty in $n$ values measurements was assigned as $\pm 0.004$.

The temperatures of the solid–nematic and nematic–isotropic phase transitions for pure and dyed liquid crystal were obtained by means of DSC method using DuPont Thermal Analyzer 990 as well as of a polarizing microscope (Leitz Orthoplan-Pol) in conjunction with a Mettler hot-stage FP-52. The experimental error by melting and clearing points determination amounted to ±0.2° and ±0.1°, respectively.

All the measurements were carried out as a function of the dyes concentration changes from $7 \cdot 10^{-3}$ M/l (~0.25% wt) to either upper limit of the dye solubility or $1.6 \cdot 10^{-1}$ M/l (~5% wt).

## 3. RESULTS AND DISCUSSION

### 3.1. The influence of the guest concentration on the order parameters of dye and liquid crystal

The order parameters of the investigated dyes in 5CB, obtained on the basis of absorption dichroic ratios, for concentration $c = 6 \cdot 10^{-2}$ M/l at room temperature ($T^* = 0.967$) and in the vicinity of the nematic–isotropic transition are given in Table II. The reduced temperature $T'^*$ is defined as follows:

$$T'^* = \frac{t + 273.2}{t'_{NI} + 273.2} \tag{1}$$

TABLE I

The dyes used in experiment

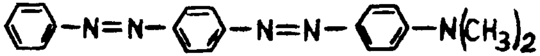
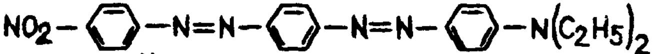
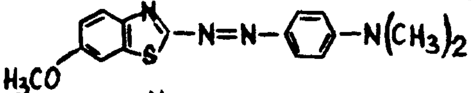
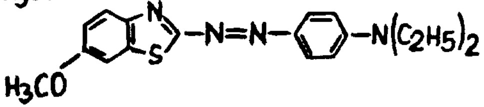
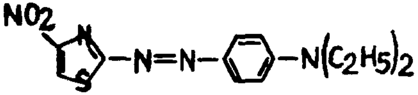
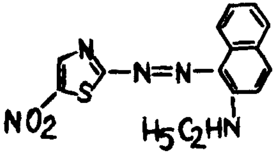
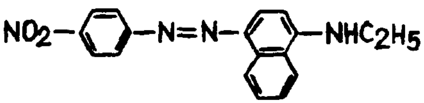
| No. | Molecular structure | M | $\lambda_{max}$ [nm] in 5CB | *l/d* |
|---|---|---|---|---|
| I |  | 329 | 495 | 2.5 |
| II |  | 402 | 538 | 2.9 |
| III |  | 328 | 512 | 2.5 |
| IV |  | 356 | 518 | 2.7 |
| V |  | 305 | 593 | 2.4 |
| VI |  | 313 | 614 | 1.4 |
| VII |  | 320 | 558 | 1.9 |

TABLE I *continued*

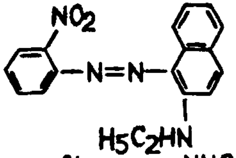
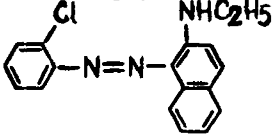
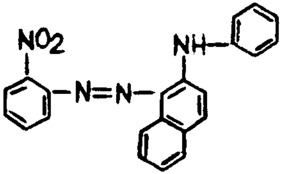
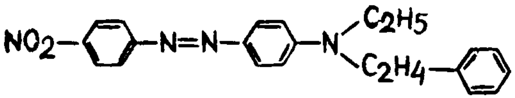
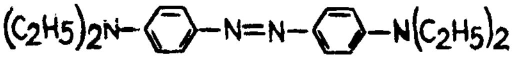
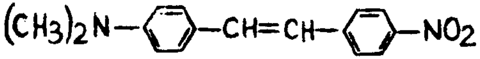
| | | | | |
|---|---|---|---|---|
| VIII |  | 320 | 533 | 1.3 |
| IX |  | 301 | 520 | 1.3 |
| X |  | 368 | 540 | 1.2 |
| XI |  | 375 | 512 | 2.5 |
| XII |  | 324 | 462 | 2.7 |
| XIII |  | 340 | 450 | 2.2 |

TABLE II

The order parameters of investigated dyes in 5CB

| No. | $\langle P_2 \rangle_G$ $T'^* = 0.967$ | $\langle P_2 \rangle_G$ at N → I transition |
|---|---|---|
| I | 0.69 | 0.45 |
| II[a] | 0.65 | 0.43 |
| III | 0.61 | 0.41 |
| IV | 0.60 | 0.40 |
| V | 0.50 | 0.30 |
| VI | 0.20 | 0.13 |
| VII | 0.15 | 0.10 |
| VIII | 0.10 | 0.05 |
| IX | 0.10 | 0.05 |
| X | 0.04 | 0.02 |
| XI | 0.38 | 0.20 |
| XII | 0.42 | 0.26 |
| XIII | 0.60 | 0.36 |

[a] $c = 2.5 \cdot 10^{-2}$ M/l; other dyes $c = 6 \cdot 10^{-2}$ M/l

where $t'_{NI}$ is the temperature of clearing point for given dye–liquid crystal mixture.

It should be noticed, that on the basis of the dichroic ratio one can estimate the order parameter referring to the transition moment direction of dyes, which is often different from that of a long molecular axis.[26] Therefore, looking at molecular structure of the investigated dyes (Table I), it seems that indescribably small values of the order parameter of dyes VIII, IX and X are a result of the great angle between a molecular axis and a direction of transition moment rather than of lack of dye orientation in the liquid crystal matrix.

It has been previously shown, that the degree of order of anthraquinone dyes[19,21] as well as of one of the azo-dye[12] diminishes with rise of the dye concentration. In order to check whether all azo-dyes behave similarly, the order parameters $\langle P_2 \rangle_G$ as a function of concentration have been measured. It has been found, that the increasing guest concentration can cause both a decrease and an increase as well as no change (within experimental error) of $\langle P_2 \rangle_G$, what is shown in Figure 1. In this figure an example of concentration dependences for azo-dyes in 5CB at three various reduced temperatures are presented. The $\langle P_2 \rangle'_G$'s were measured up to concentration of $6.6 \cdot 10^{-2}$ M/l. The measurements for higher concentration are very difficult because of high absorption intensity of the samples.

The host order parameter $\langle P_2 \rangle_H$ was determined for samples both of pure liquid crystal and of liquid crystal with dye. Unfortunately,

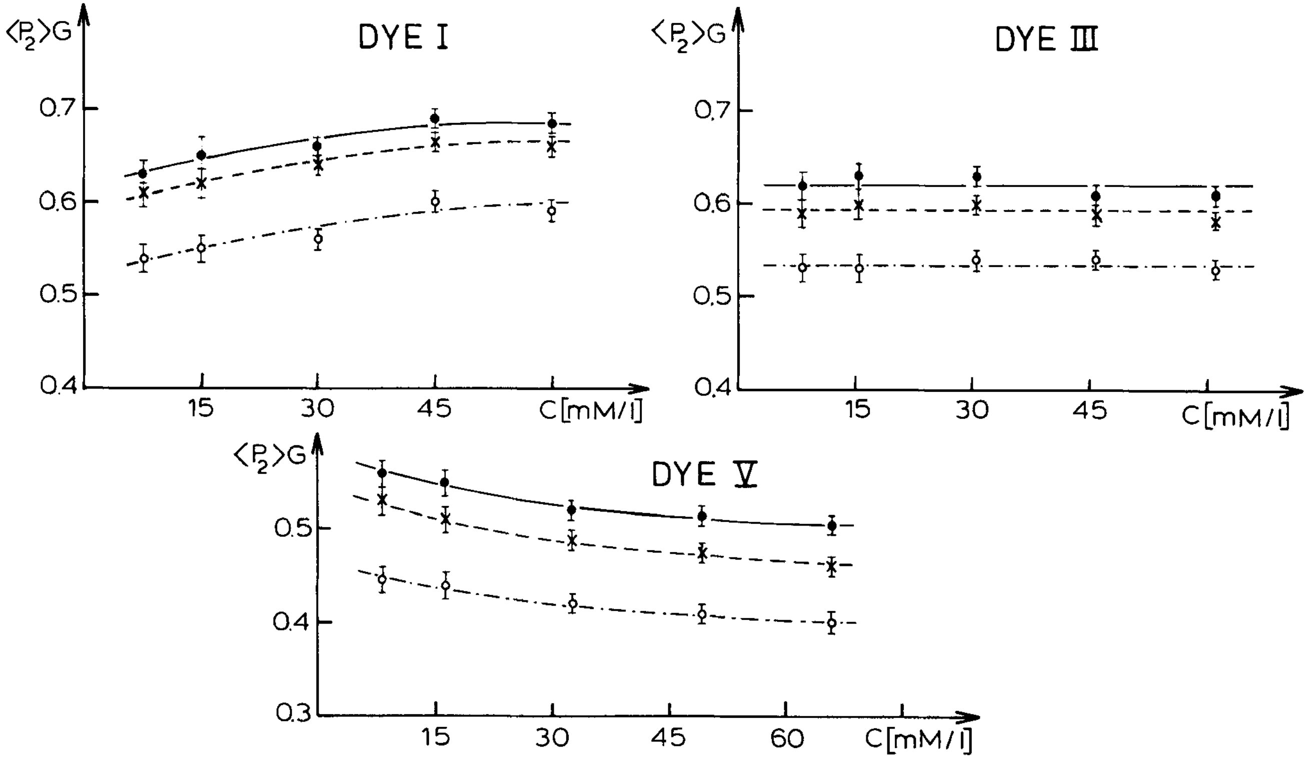


FIGURE 1 The exemplary changes of the order parameter $\langle P_2 \rangle_G$ with the dye concentration at various reduced temperatures: $T'^* = 0.967$ (——), $T'^* = 0.977$ (---), $T'^* = 0.993$ (-·-·) for azo-dyes in 5CB.

because of absorbing the sodium light by most of the used dyes, the measurements of the refractive indices for yellow and orange dyes were only possible. The results of these measurements are presented in Figure 2, where the temperature dependence of the refractive indices for pure 5CB as well as for 5CB with dye I (the best oriented dye) and with dye IX (the dye with small $\langle P_2\rangle_G$) are shown. The dye concentration was $4.5 \cdot 10^{-2}$ M/l. On the basis of birefringence data the host order parameter was evaluated. Figure 3A shows the temperature dependence of $\langle P_2\rangle_H$ for pure 5CB and for those dye–liquid crystal mixtures as in Figure 2. The small, but measurable changes of the host ordering after dye addition are observed. The experimental error in the host order parameter values was estimated as $\pm 0.015$. Therefore, the results listed in Table III are maybe not too reliable, but they show some trend to change of the liquid crystal molecules orientation with increasing dye concentration.

Comparing the host and guest order parameter data with $l/d$ values of the investigated dyes one can see that there exist broad correlation between sizes of the dye molecules and mutual relation between $\langle P_2\rangle_G$ and $\langle P_2\rangle_H$. However, the $\langle P_2\rangle_G$ values of dyes XI or XII, for example, suggest that factors other than molecular geometry of dye play also some role. The important factor seems to be the anisotropic guest interaction with the host, which is various for different dyes. The ratio $\langle P_2\rangle_G/\langle P_2\rangle_H$ can be a measure of these interactions. From results presented in this paper one can see, that if $\langle P_2\rangle_G/\langle P_2\rangle_H > 1$, then both guest and host ordering do not change or even increase with rise of dye concentration (see for example dyes I and III). In the case, where $\langle P_2\rangle_G/\langle P_2\rangle_H < 1$ (dyes V, IX)—the degree of molecular order falls off when the dye concentration increases, what has been also previously found for dye V in 5CB using Raman spectroscopy.[12]

Figure 3B shows the dye and liquid crystal order parameters measured as a function of reduced temperature for the sample containing dye I in 5CB ($c = 4.5 \cdot 10^{-2}$ M/l). As it follows from this figure the difference between guest and host molecular ordering is changed with the increasing temperature. The changes can be more exactly seen in Table IV, where the ratios $\langle P_2\rangle_G/\langle P_2\rangle_H$ at various temperatures for mixtures of 5CB with dye I and dye V, as an example, are presented. In the case of dye V the values of $\langle P_2\rangle_H$ were taken for pure 5CB.

It is seen from this table, that dye I having $\langle P_2\rangle_G/\langle P_2\rangle_H$ appreciable higher than 1 shows that $\langle P_2\rangle_G/\langle P_2\rangle_H$ increases with increasing temperature, whereas the lack of such dependence is observed for dye V having $\langle P_2\rangle_G/\langle P_2\rangle_H < 1$. This means that the dyes with $\langle P_2\rangle_G >$

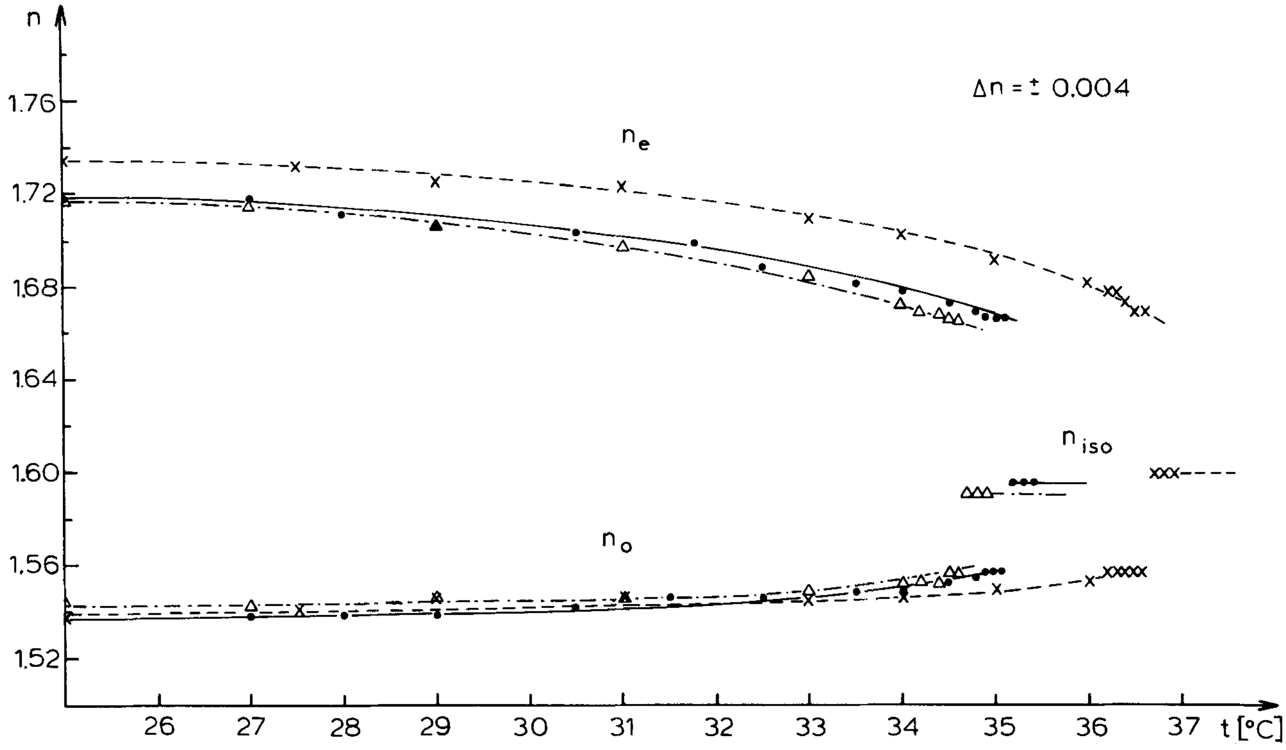


FIGURE 2 The refractive indices *versus* temperature for: pure 5CB (——), 5CB with dye I (---), 5CB with dye IX (-·-·-). The dye concentration $c = 4.5 \cdot 10^{-2}$ M/l.

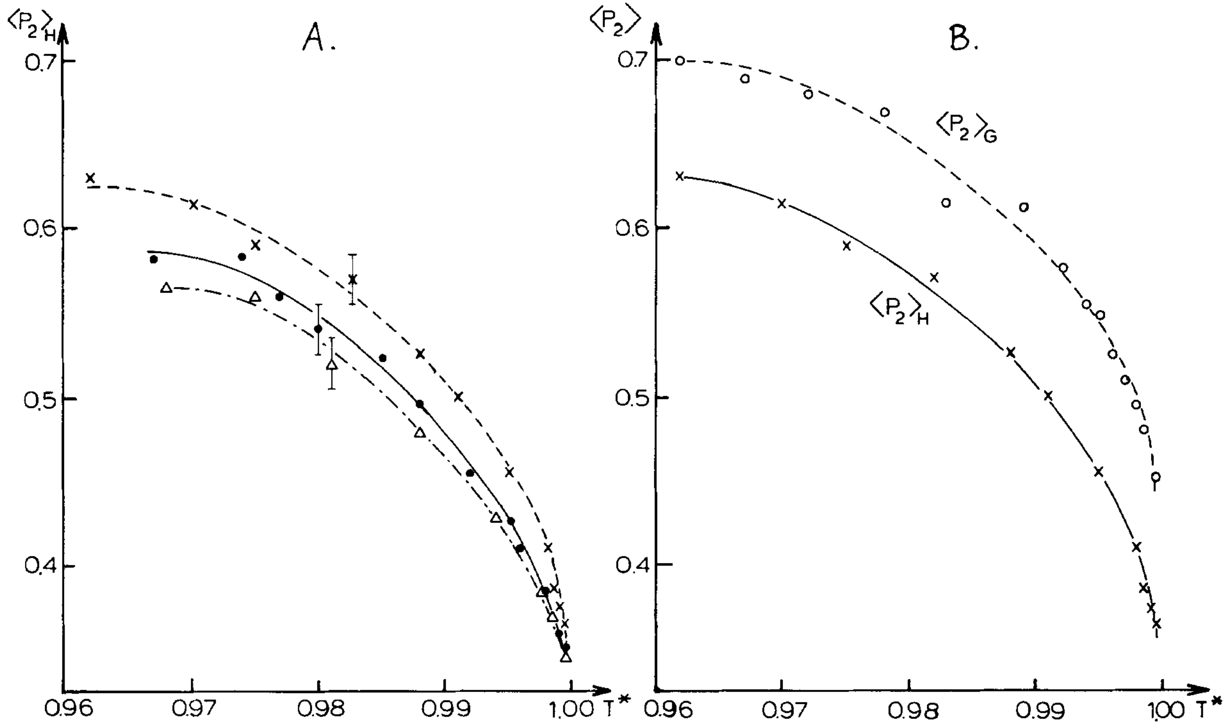


FIGURE 3 A. The host order parameter $\langle P_2 \rangle_H$ *versus* reduced temperature for: pure 5CB (——), 5CB with dye I (---) and 5CB with dye IX (-··-). The dye concentration $c = 4.5 \cdot 10^{-2}$ M/l. B. The host $\langle P_2 \rangle_H$ and guest $\langle P_2 \rangle_G$ order parameter as a function of reduced temperature in the sample containing dye I in 5CB ($c = 4.5 \cdot 10^{-2}$ M/l).

TABLE III

The change of the host order parameter after dye I addition

| | $\langle P_2\rangle_H$ | | |
|---|---|---|---|
| $c$ [M/l] | T'* = 0.967 | T'* = 0.977 | T'* = 0.993 |
| 0 | 0.582 | 0.559 | 0.448 |
| $7.5\ 10^{-3}$ | 0.582 | 0.555 | 0.455 |
| $1.5\ 10^{-2}$ | 0.595 | 0.564 | 0.464 |
| $3.0\ 10^{-2}$ | 0.609 | 0.564 | 0.464 |
| $4.5\ 10^{-2}$ | 0.623 | 0.585 | 0.475 |
| $6.0\ 10^{-2}$ | 0.632 | 0.590 | 0.482 |

$\langle P_2\rangle_H$ are more resistant to the thermal fluctuations compared to the host liquid crystal.

### 3.2. The phase transitions of the guest–host mixtures

As can be seen from Figure 2, the addition of the dye to the liquid crystalline matrix changes the nematic–isotropic transition temperature, causing either decrease or increase of the clearing point of pure liquid crystal. Moreover, the experiments done in this study showed that presence of the guest leads to the formation of a two-phase region, in which coexist both nematic and isotropic phase. Such a region was previously observed for various solute of different sizes and shapes, which depressed the clearing point of pure liquid crystal.[6–11,16] However, until now no existence of two-phase region for elongated dye molecules, which can also increase the transition temperature, was found.

TABLE IV

The ratio of the order parameter of dye ($\langle P_2\rangle_G$) and the order parameter of liquid crystal ($\langle P_2\rangle_H$) *versus* temperature.

| | $\langle P_2\rangle_G/\langle P_2\rangle_H$ | |
|---|---|---|
| T'* | dye I, $c = 4.5\cdot10^{-2}$ M/l | dye V, $c = 3.3\cdot10^{-2}$ M/l |
| 0.965 | 1.11 | 0.92 |
| 0.970 | 1.12 | 0.89 |
| 0.975 | 1.13 | 0.88 |
| 0.980 | 1.13 | 0.88 |
| 0.985 | 1.14 | 0.89 |
| 0.990 | 1.16 | 0.92 |
| 0.995 | 1.20 | 0.96 |

The exemplary dependences of the nematic–isotropic transition temperature on dye concentration obtained for dye III and dye X in 5CB are illustrated in Figure 4; there $x$ is dye mole fraction and $T^* = (t'_{NI} + 273.2)/(t_{NI} + 273.2)$ is reduced temperature, where $t_{NI}$ is clearing temperature of the pure host. The $T^*_N$ and $T^*_I$ are temperatures, at which the first isotropic drop appears and the last nematic drop disappears, respectively, by heating of guest–host mixture.

As it follows from Figure 4, the region of two-phase coexistence for the azo-dye/5CB mixtures is very narrow (~0.5° at $c = 9 \cdot 10^{-2}$ M/l). The results obtained in previously paper[12] showing the wide

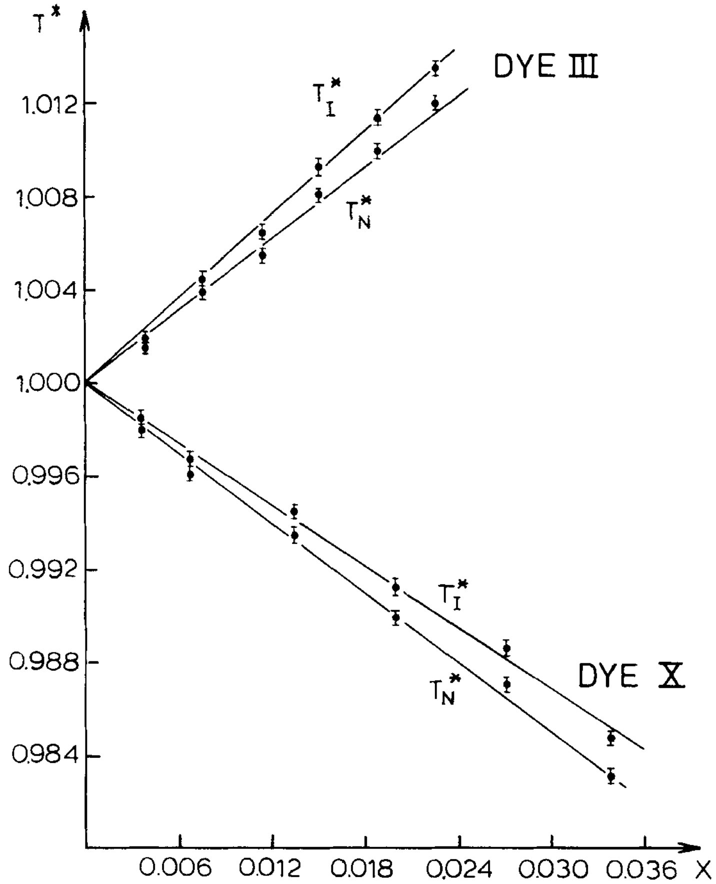


FIGURE 4 The reduced temperature (T*)—dye mole fraction (x) diagram for dye III and dye X in 5CB.

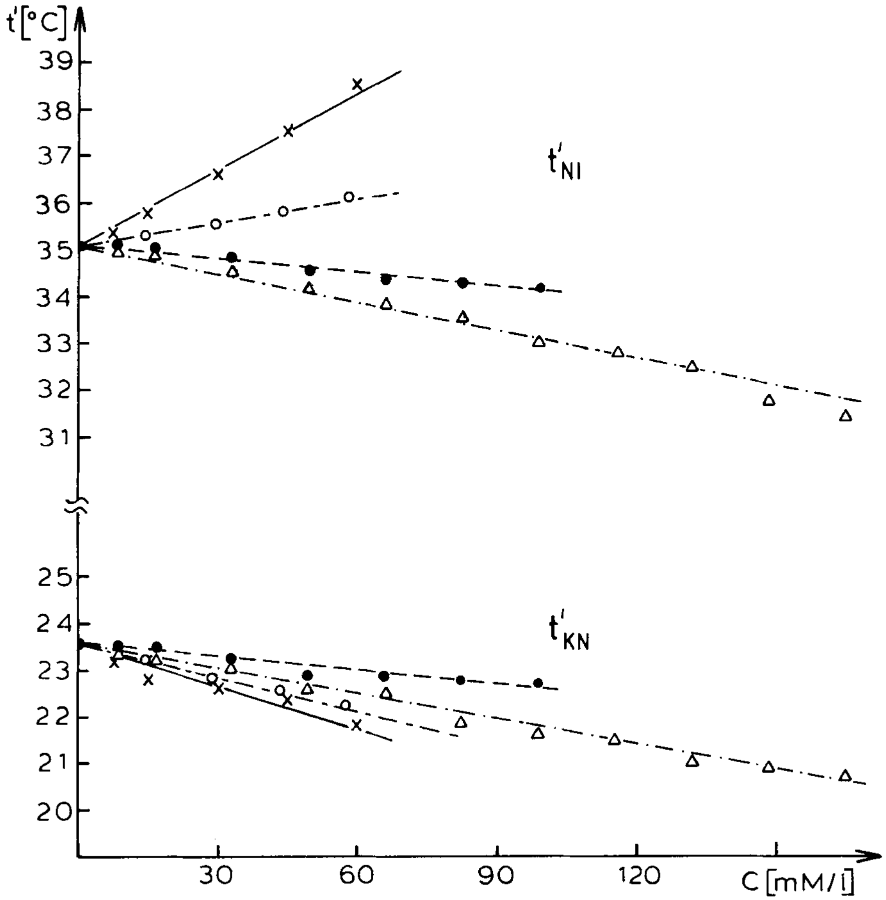


FIGURE 5 The changes of the transition temperatures of dyes: I (——), V (---), IX (-·-·) and XIII (– – – –) in 5CB with dye concentration.

two-phase region for one of azo-dye in 5CB seems to be not too plausible.

The nematic–isotropic $t'_{NI}$ and the solid–nematic $t'_{KN}$ transition temperature *versus* dye concentration for several choice dyes in 5CB are presented in Figure 5, whereas the shifts in melting ($\Delta t_{KN} = t'_{KN} - t_{KN}$) and clearing ($\Delta t_{NI} = t'_{NI} - t_{NI}$) points for all investigated dyes at $6 \cdot 10^{-2}$ M/l concentration are given in Table V. $t'_{NI}$ is now the average value of temperatures at which the two-phase region begins and ends.

The transition temperatures of pure liquid crystal 5CB, determined in this study, are following: $t_{KN}$ = 23.4°C and $t_{NI}$ = 35.1°C. From

TABLE V

Thermodynamic data on mixtures of the investigated dyes in 5CB
($c = 6 \cdot 10^{-2}$ M/l)

| No. | $\Delta t_{KN}$ | $\Delta t_{NI}$ | $\beta_N$ | $\beta_I$ | $\beta_N^*$ | $\beta_I^*$ | $\gamma_N^*/\gamma_I^*$ |
|---|---|---|---|---|---|---|---|
| I | −1.6 | +3.5 | +0.68 | +0.79 | +0.67 | +0.80 | 0.83 |
| II[a] | −1.0 | +1.1 | +0.52 | +0.63 | +0.53 | +0.62 | 0.87 |
| III | −1.0 | +2.7 | +0.53 | +0.62 | +0.53 | +0.62 | 0.87 |
| IV | −0.4 | +1.1 | +0.23 | +0.28 | +0.25 | +0.26 | 0.94 |
| V | −0.5 | −0.7 | −0.16 | −0.12 | −0.14 | −0.13 | 1.04 |
| VI | −1.1 | −1.4 | −0.32 | −0.24 | −0.29 | −0.27 | 1.08 |
| VII | −1.5 | −1.5 | −0.34 | −0.28 | −0.32 | −0.33 | 1.08 |
| VIII | −1.4 | −1.8 | −0.43 | −0.38 | −0.42 | −0.39 | 1.11 |
| IX | −0.9 | −1.3 | −0.25 | −0.23 | −0.24 | −0.23 | 1.06 |
| X | −1.2 | −1.8 | −0.48 | −0.40 | −0.46 | −0.42 | 1.13 |
| XI | −0.8 | −3.4 | −0.87 | −0.75 | −0.89 | −0.73 | 1.22 |
| XII | −0.5 | −1.6 | −0.38 | −0.29 | −0.36 | −0.31 | 1.09 |
| XIII | −0.6 | +1.0 | +0.20 | +0.22 | +0.20 | +0.22 | 0.95 |

[a] $c = 2.5 \cdot 10^{-2}$ M/l

Figure 5 and Table V it is seen, that although the clearing point of the liquid crystal after dye adding either diminishes or rises, the melting point is always decreasing. This means that some dyes can destroy and others stabilize the mesophase region of the nematic solvent.

The indicators of the order-destruction or the order-enhancement of the nematic phase by guest are the slopes of the reduced temperatures $T_N^*$ and $T_I^*$ with change of the solute mole fraction, defined as follows:

$$\beta_N = \frac{dT_N^*}{dx} \tag{2a}$$

and

$$\beta_I = \frac{dT_I^*}{dx} \tag{2b}$$

The positive β means the ability of a solute to enhancing, and negative β to destroying the host nematic phase.

According to the literature,[6] at very low solute concentration, the limiting slopes of the nematic phase boundary line $\beta_N^*$ and the isotropic phase boundary line $\beta_I^\infty$ are connected with the solute activity coefficients by relations:

$$\beta_N^\infty = \left(1 - \frac{\gamma_N^\infty}{\gamma_I^\infty}\right)\left(\frac{R}{\Delta S_{NI}}\right), \tag{3a}$$

$$\beta_I^\infty = \left(\frac{\gamma_N^\infty}{\gamma_I^\infty} - 1\right)\left(\frac{R}{\Delta S_{NI}}\right), \tag{3b}$$

where R is gas constant, $\Delta S_{NI}$ is nematic–isotropic transition entropy of the pure nematic solvent, and $\gamma_N^\infty$ and $\gamma_I^\infty$ are the infinite-dilution (Henry's law region) solute activity coefficients in the nematic and the isotropic phases, respectively.

In order to determine the ratio of $\gamma_N^\infty/\gamma_I^\infty$, the experimentally obtained $\beta$ values have been corrected to infinite dilution using procedure described by Kronberg *et al.*[34] It assumed the $\Delta S/R$ value for 5CB as 0.253, following reference.[7]

The values of $\beta_N$ and $\beta_I$, the corrected $\beta_N^\infty$ and $\beta_I^\infty$ slopes as well as ratios $\gamma_N^\infty/\gamma_I^\infty$ for investigated dyes in 5CB are gathered in Table V. For the $\beta$ parameters vary somewhat with dye concentration this table gives the values obtained at $c = 6 \cdot 10^{-2}$ M/l, except dye II, solubility of which is very poor.

The smaller ratio $\gamma_N^\infty/\gamma_I^\infty$ implies greater compatibility with the nematic phase of the host and *vice versa*, thus correlation between the activity coefficients and the ordering of the guest by the host would be anticipated.

Comparing the results from Table V with those from Table II one can see, that the dyes which show $\langle P_2\rangle_G > \langle P_2\rangle_H$ have $\gamma_N^\infty/\gamma_I^\infty < 1$, thus they are able to correlate their long molecular axes alignment parallel to the long axes of liquid crystal molecules. These dyes stabilize the nematic host causing the broadening of the mesophase region. However, for cases where $\langle P_2\rangle_G < \langle P_2\rangle_H$ the dye added to the liquid crystal depresses the nematic–isotropic phase transition temperatures, leading to the destruction of the host mesophase.

### 3.3. The comparison of the experimental results with the theoretical predictions

In this section the relation between the behaviour of the liquid crystal–dye mixture at nematic–isotropic transition and the order parameter as well as molecular geometry of guest is examined theoretically.

On the basis of the Maier-Saupe mean field theory for binary mixture[35] the expression for the ratio of the infinite-dilution solute activity coefficients in the vicinity of the clearing point is following:

$$\ln\left(\frac{\gamma_N^\infty}{\gamma_I^\infty}\right) = \frac{\Delta S_{NI}}{R}\left\{\left(\frac{v_2}{v}\right) - \left(\frac{b_{12}}{b_{11}}\right)^2\right\}, \tag{4}$$

where $v$ and $v_1$ are, respectively, the solute and solvent molecular volumes, while ratio $b_{12}/b_{11}$ is a measure of the relative strength of solvent–solute and solvent–solvent intermolecular attractive interactions. The $b_{12}/b_{11}$ ratio may be easily estimated from the measurements of $\langle P_2\rangle_G/\langle P_2\rangle_H$ at nematic–isotropic transition.[35]

Knowing the $\gamma_N^\infty/\gamma_I^\infty$ values, the slopes $\beta_N^\infty$, $\beta_I^\infty$ and the shifts in the clearing point on adding dye ($\Delta T_N^*$, $\Delta T_I^*$) can be calculated from Equations (3) and (2), respectively.

Because of the lack of molecular volume data for the investigated dyes, the molecular weight $M_1$ and $M_2$ as measured of, respectively, the solvent and solute molecular sizes in the first trying on were used. The results of calculations revealed, that there is some correlation between the orientation of guest in liquid crystal and the shift in the transition temperature: the mixtures, where dye molecules show greater compatibility with host molecules have less negative or positive $t_{NI}$, similarly as it was observed in the experiment. However, the results of the theoretical calculations differ significantly from those obtained in experiment both in magnitude and in sign. The situation appears as if the values $v_2/v = M_2/M_1$ were much larger than the real ratios of molecular volumes. Taking $v_2/v$ as an adjustable parameter, agreement with experiment is obtained for $v_2/v$ values, which are very close to $m_2/m_1$, where $m = l/d$. Thus in the next fitting on, the molecular length to breadth ratio was used as a measured of the guest and host sizes. The $m_1$ of monomeric 5CB molecule was evaluated taking into account the flexibility of the alkyl chain[26] and it was assigned as 2.5.

Because the dye order parameter, needed to $\gamma_N^\infty/\gamma_I^\infty$ calculation, changes with guest concentration, clearly it is not possible to reproduce here in full all the data taken in this study. Figure 6 gives results on mixtures showing the largest concentration dependence of $\langle P_2\rangle_G$.

In Figure 6 the measured (circles) and calculated, assuming $v_2/v = m_2/m_1$ (triangles), temperature shifts $\Delta T_N^*$ and $\Delta T_I^*$ *versus* dye concentration for dye I and dye V in 5CB are presented. Table VI, however, gives results of $\beta_N^\infty$ and $\beta_I^\infty$ obtained from experiment as well as from theoretical calculations taking the molecular weight in one

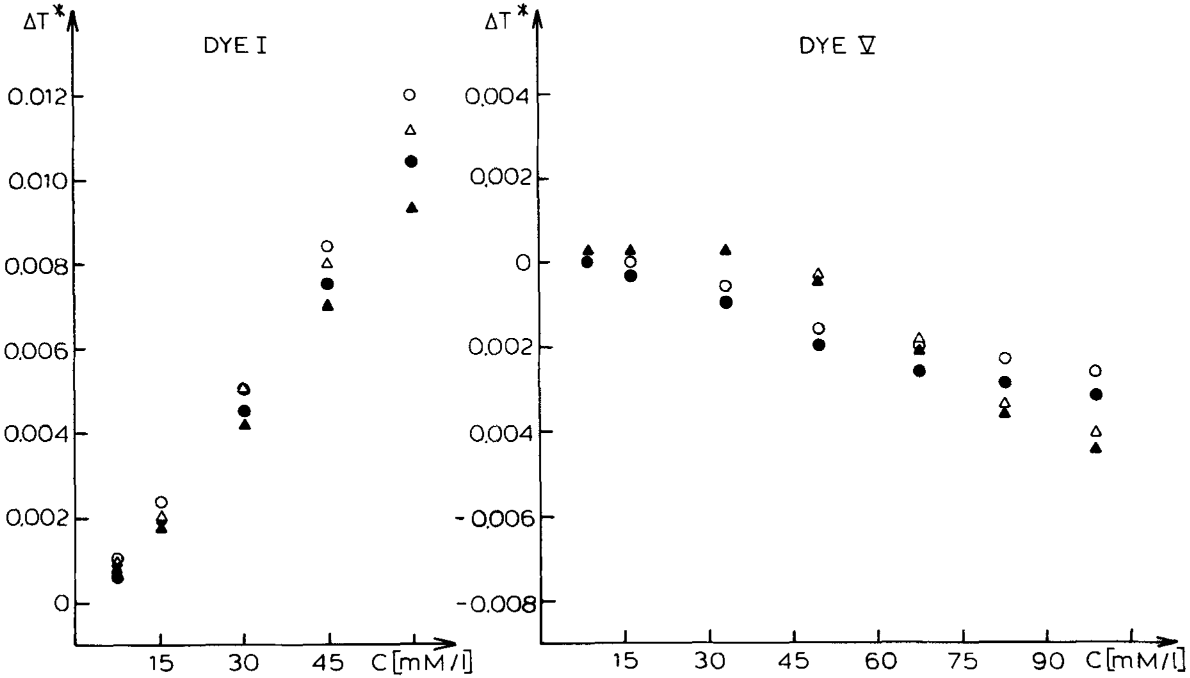


FIGURE 6 The experimental (circles) and theoretical (triangles) shifts of the clearing temperature *versus* dye concentration for dye I and dye V in 5CB. The filled and open marks denote $\Delta T_N^*$ and $\Delta T_I^*$, respectively.

TABLE VI

Comparison of experimental $\beta_N^\infty$ and $\beta_I^\infty$ values with theoretical calculations

| | | | Theory | | | |
|---|---|---|---|---|---|---|
| | Experiment | | $\frac{\nu_2}{\nu}=\frac{M_2}{M_1}$ | | $\frac{\nu_2}{\nu}=\frac{M_2}{M_1}$ | |
| No. | $\beta_N^\infty$ | $\beta_I^\infty$ | $\beta_N^\infty$ | $\beta_I^\infty$ | $\beta_N^\infty$ | $\beta_I^\infty$ |
| I | +0.56 | +0.65 | +0.25 | +0.26 | +0.53 | +0.62 |
| II | +0.53 | +0.62 | −0.07 | −0.17 | +0.34 | +0.37 |
| III | +0.46 | +0.52 | −0.02 | −0.02 | +0.35 | +0.39 |
| IV | +0.25 | +0.26 | −0.12 | −0.11 | +0.24 | +0.25 |
| V | −0.10 | −0.08 | −0.41 | −0.37 | −0.04 | −0.03 |
| VI | −0.32 | −0.30 | −1.30 | −0.98 | −0.42 | −0.38 |
| VII | −0.32 | −0.30 | −1.41 | −1.04 | −0.74 | −0.62 |
| XI | −0.85 | −0.70 | −1.37 | −1.02 | −0.76 | −0.63 |
| XII | −0.36 | −0.31 | −0.83 | −0.69 | −0.56 | −0.49 |
| XIII | +0.19 | +0.22 | −0.32 | −0.30 | +0.19 | +0.20 |

case and ratio $l/d$ in other one as a measure of the liquid crystal and dye molecules sizes. The results presented there are averages because both experimental and calculated values of $\beta_N^\infty$ and $\beta_I^\infty$ are changing with dye concentration. In this table the results for dyes VIII, IX and X are missing for in these cases the comparison between experiment and theory cannot be done because of the difficulty in $b_{12}/b_{11}$ evaluation (see Section 3.1).

The results given in Figure 6 and Table VI indicate that assuming $v_2/v = m_2/m_1$ one can obtain the satisfactory agreement of the theoretical calculations with the experimental data, both in determination of the sign and magnitude of $\beta^\infty$ and $\Delta T^*$ as well as in prediction of the range of the two-phase coexistence region.

The experimental results obtained in this study were also compared with theoretical calculations done on the basis of the second model generally useful for investigating nematic–isotropic transition in the dilute solution region of binary mixtures, namely lattice model.[35,36] This model, in its original form, emphasize the role of anisotropic intermolecular repulsion, that is packing or steric effects, neglecting the anisotropic intermolecular attraction.

Compared in Figure 7 are the experimental values of $\beta_N^\infty$ obtained in this study (points) and those calculated from the lattice models. The prediction of the lattice model theory for binary mixtures of hard, completely rigid rods[36] is given by curve 1, whereas curve 2 represents the results calculated from lattice model take account of the fact that the terminal chain of liquid crystal molecules is more

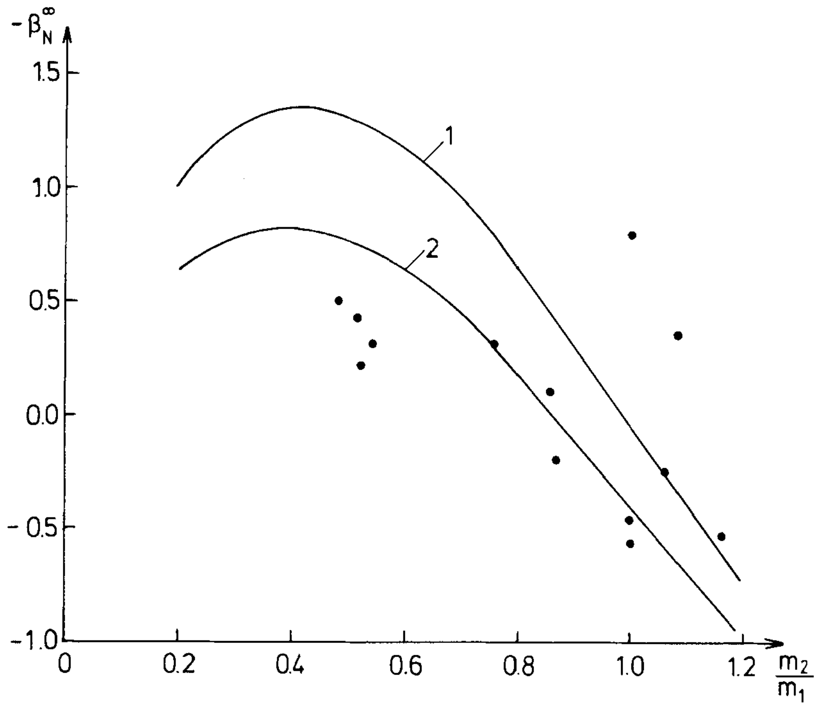


FIGURE 7 The slope $\beta_N^\infty$ *versus* $m_2/m_1$. Circles: experimental results of this study; curve 1: lattice model results[36] for mixtures of rigid rods; curve 2: lattice model results[37,38] for mixtures of rigid rod solutes and solvent molecules composed of rigid core and semiflexible tail.

flexible than the remainder of these.[37,38] Although the both models correctly predicts the trend of increasing $\beta_N$ with increasing $m_2/m_1$ ratio, the agreement of the theory with the experiment is unsatisfactory. However, it is worth noting that the better agreement with experiment occurs for curve 2, what demonstrates the important role of solvent end-chain flexibility.

Looking at the results from Table VI and Figure 6 as well as Figure 7 one can clearly see, that calculations basing on the mean-field model give better fit to the experimental results as compared with lattice model theory. As is evident from Figure 7 the largest difference between experimental and from lattice models calculated values of $\beta_N^\infty$ occurs for dyes XI and XII. The reason for these results is that these dyes despite of their significant lengths have very low order parameter in 5CB (Table II), what means that their compatibility with nematic host is very poor. This can be interpreted as showing that the neglect of attractive interactions and the anisotropy thereof in lattice models leads to disagreement between theoretical and experimental results.

## 4. CONCLUSIONS

The results of the measurements of some optical and thermodynamical parameters for the solutions of the azo-dyes in the nematic liquid crystal 5CB have been presented. The study of the order parameter revealed two effects: (i) the orientation both guest and host molecules is affected by change of the dye concentration; (ii) the concentration dependence is various for different dyes and it is connected with the mutual connection between guest ($\langle P_2\rangle_G$) and host ($\langle P_2\rangle_H$) order parameter.

The thermodynamic data showed that azo-dyes can either stabilize or destroy the nematic phase of host. The melting point decreases always after dye addition, whereas the sign and magnitude of $\Delta t_{NI}$ depend on the guest compatibility with the host and on the molecular size and shape of the solute as well. The occurrence of the theoretically predicted two-phase region at nematic–isotropic transition was observed. This region is quite narrow for elongated dyes molecules, especially at low concentration, therefore it is not surprising that most workers[17–19,24] have failed to observe it previously.

The comparison of the experimental results with values predicted on the basis of two models mainly used for investigation of nematic–isotropic transitions in binary mixtures, namely molecular field theory of Maier–Saupe and lattice model, revealed that there is the better agreement of the experiment with the former model, which regard not only molecular geometry of the guest, but also guest interaction with anisotropic host.

Finally, it is worth noting that in order to describe the behaviour of a guest–host mixture at the nematic–isotropic transition, this means the sign and the approximate magnitude of $\Delta t_{NI}$, as well as the occurrence and the extent of the two-phase region, it is not necessary to speculate on the additional interactions, as for example dipole/induced-dipole force.[17,39] It is only needed to take into account the following factors: (i) length to breadth ratio $l/d$ of solute, which is a measure of steric effects, (ii) dispersive attraction measured through $\langle P_2\rangle_G/\langle P_2\rangle_H$ ratio, (iii) concentration dependence of the guest and host molecular order and (iv) flexibility of the end-chain of the liquid crystal molecules.

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